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We have constructed and tested new higher-temperature ceramic ( $\text{ZrO}_2$  and  $\text{SiC}$ ) pyrolysis nozzles that can operate continuously at  $1700^\circ\text{C}$  for several hours. The two successful designs were used to generate intense ( $10^{16}\text{sec}^{-1}$ ) beams of hydrocarbon radicals and carbenes by thermal decomposition of appropriate precursors that were inaccessible with our previous  $\text{Al}_2\text{O}_3$  designs. The new nozzle design makes possible quantitative sequential homolytic cleavage of a C-Br bond to generate a radical, or two C-Br bonds to generate a carbene. We generated a molecular beam of propadienylidene ( $\text{l-C}_3\text{H}_2$ ) from 1,3-dibromopropyne in this fashion.

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by

Peter Chen

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# TECHNICAL REPORT FOR GRANT #N00014-91-J-1012

## *Supersonic Pyrolysis Jets for Diamond Film Deposition*

**Peter Chen**  
**Assistant Professor of Chemistry**  
**Harvard University**

**May 12, 1991**

### **Introduction**

Recent progress in the production of high-intensity supersonic free jets of hydrocarbon radicals (e.g.  $\text{CH}_n$ ,  $\text{C}_2\text{H}_n$ ,  $\text{C}_3\text{H}_n$ ), has made it possible to investigate the growth mechanism of diamond and diamond-like carbon by bombardment of a substrate with a well-characterized supersonic flow of defined radicals. This report details the first phase of the project, encompassing source design, and the engineering of specific radical precursors. Efficacy of both source and precursor is determined spectroscopically. Construction of a vacuum chamber in which the precursors and nozzles will be used to attempt deposition of diamond-like carbon or diamond itself from a free jet of radicals is underway. We expect the chamber to be working by the end of summer 1991. Progress until then consists of the following areas in which key methodological approaches are worked out.

### **Recent Progress in Nozzle Design**

Our previous externally-heated,  $\text{Al}_2\text{O}_3$  pyrolysis nozzles suffered from several limitations which would limit their usefulness in any deposition application: (i) A practical upper limit of  $1500^\circ\text{C}$  precluded complete pyrolysis for molecules for which the activation energy for reaction exceeded  $\approx 50$  kcal/mol, and (ii) the wirewound  $\text{Al}_2\text{O}_3$  tube nozzles had relatively short lifetimes at the higher operating temperatures. The

lifetime was sufficient for some spectroscopic studies, but would limit other uses, such as deposition.

To circumvent these problems, we have constructed nozzles from electrically conducting ceramics that can be resistively heated directly. Heat transfer is no longer a problem, and the two materials chosen, stabilized  $\text{ZrO}_2$  and recrystallized SiC, both have negative temperature coefficients of resistance, e.g. electrical resistance decreases with increasing temperature. This property ensures uniform temperature over the entire heated length of the nozzle. Schematics of the  $\text{ZrO}_2$  and SiC nozzles are shown in Figures 1 and 2, respectively. These have achieved stable operation at  $1700^\circ\text{C}$  (by optical pyrometry) for several hours. Total conversion of precursors for which direct homolysis of bonds as strong as 75 kcal/mol is required can be achieved with these new designs.

### **Recent Progress in Radical Precursors**

A logical first choice for radicals is  $\text{CH}_3$ . While  $\text{CH}_3$  can be made pyrolytically from  $\text{CH}_3\text{I}$ , it is desirable to have a halogen-free source. Di-(*tert*-butyl)-peroxide, upon pyrolysis, produces  $\text{CH}_3$  and acetone. In the process, we have found that, with the newer, higher-temperature nozzles, we could reduce acetone to  $\text{CH}_3$  and CO. In all cases, bimolecular radical products could be suppressed and were not observed in the jet. This may be very useful for deposition on a substrate with which CO is unreactive.

Other likely precursors for high-density carbon films may be vinylidene-type carbenes that can do direct insertion reactions into surface bonds. Such insertion reactions would obviate the need for prior surface activation by H-abstraction. The proposed role of acetylene in diamond film growth may derive from the facile acetylene-vinylidene equilibrium at high temperatures. We have explored precursors to the kinetically-stable vinylidene carbene, propadienylidene [ $\text{C}_3\text{H}_2$ ], as a potentially surface-reactive species. We have synthesized a large range of precursors, shown in Figure 3,

and assayed them by vacuum-uv photoionization mass spectroscopy of the pyrolysate. We found that one precursor, 1,3-dibromopropyne, that is converted exclusively to the carbene by two sequential C-Br bond homolyses. Photoionization mass spectra, without and with pyrolysis, are shown in Figure 4. Further work using this molecule for deposition is now planned.

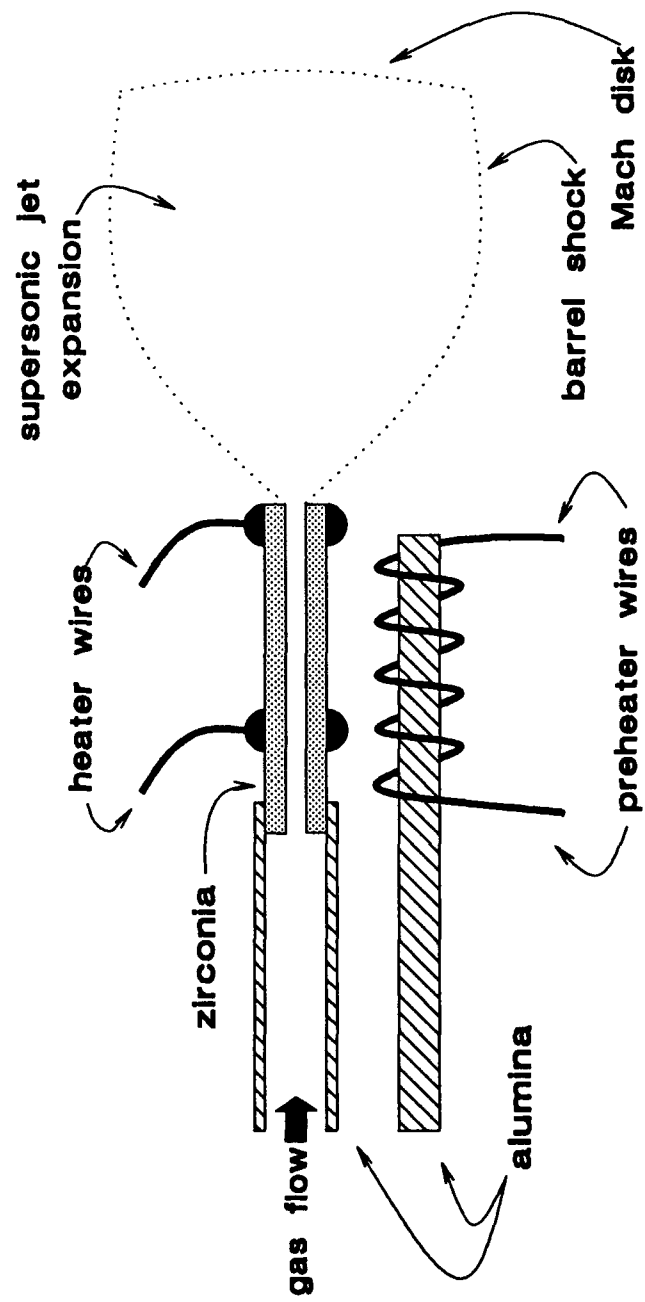
## FIGURE CAPTIONS

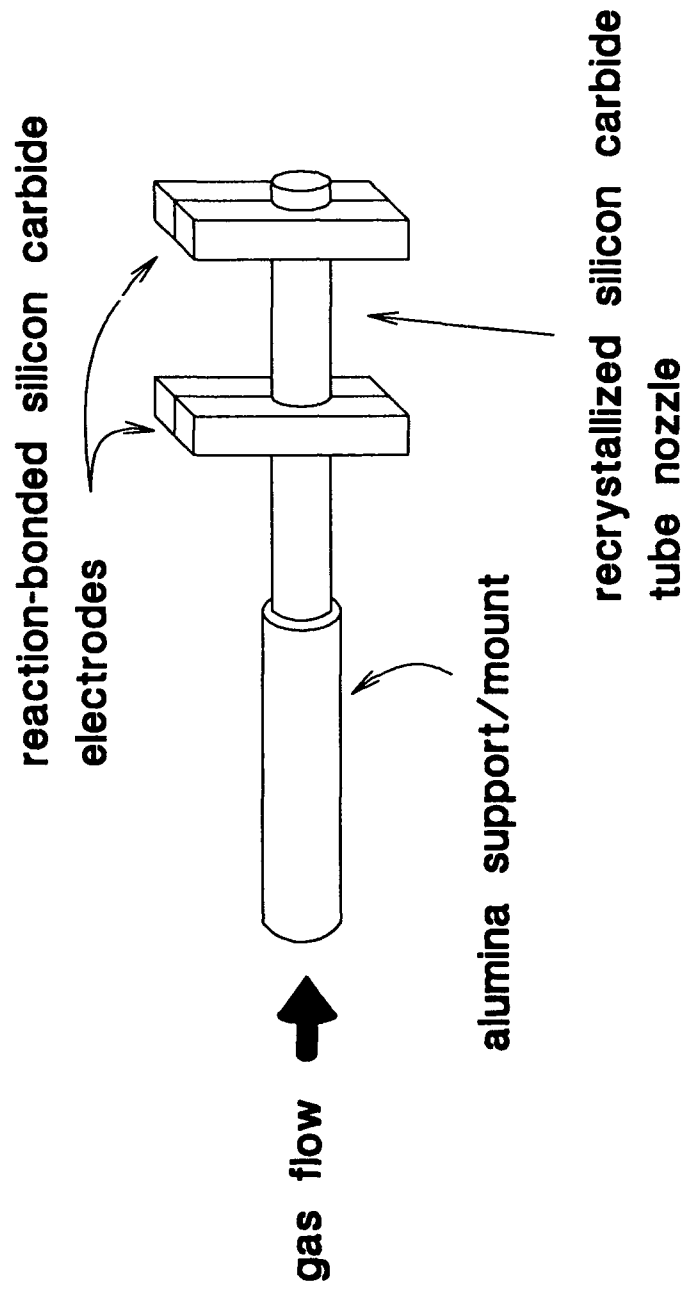
Figure 1. Schematic of  $\text{ZrO}_2$  pyrolysis nozzle. Inner diameter of the nozzle is 1.0 mm, and the heated section between the electrodes is 10.0 mm in length. Maximum continuous operating temperature is 1750°C. Electrodes are platinum wetted onto the oxide surface.

Figure 2. Schematic of SiC pyrolysis nozzle. Inner diameter of the nozzle is 1.0 mm, and the heated section between the electrodes is 10.0 mm in length. Maximum continuous operating temperature is 1700°C. Electrodes are electric-discharge-machined from reaction-bonded SiC slugs and press-clamped onto the recrystallized SiC tube with a thin layer of graphite in between. The electrode material is a much better electrical conductor than the tube material, so the electrodes remain cool even when the tube is incandescent.

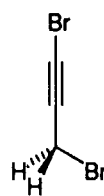
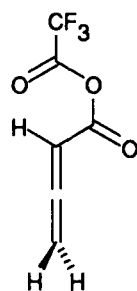
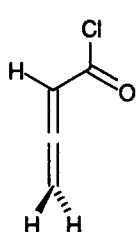
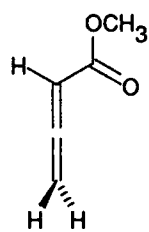
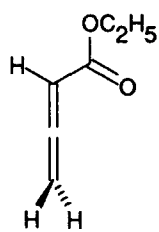
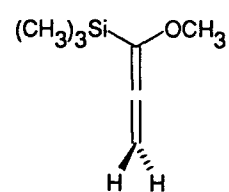
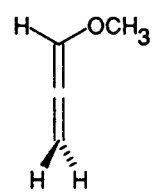
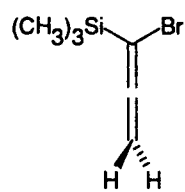
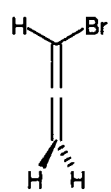
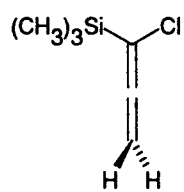
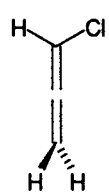
Figure 3. Potential pyrolytic precursors to propadienylidene [ $\text{C}_3\text{H}_2$ ] synthesized since January 1991. 1,3-Dibromopropyne gave the best results upon pyrolysis.

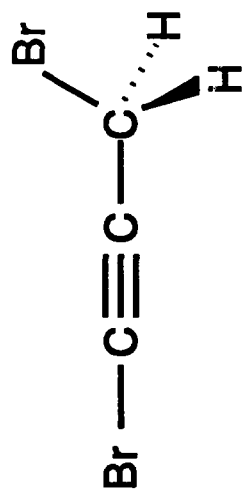
Figure 4. 10.49 eV vacuum-uv photoionization mass spectra of unpyrolyzed and pyrolyzed 1,3-dibromopropyne, seeded in 2 atm helium carrier gas. Conversion to the carbene is quantitative with no detectable bimolecular reactions in the gas-phase. Estimated flux of the carbene is  $10^{16} \text{ sec}^{-1}$  during the gas pulse. The carbene is a multifunctional molecule which may give direct insertion into surface bonds,











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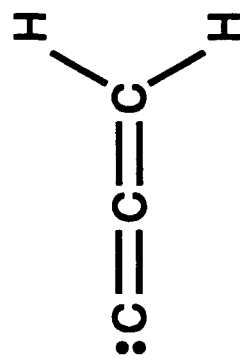
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Heat off

benzene as a  
mass calibrant

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Heat on

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